OH $A^2\Sigma-X^2\Pi(0,0)$ BAND ROTATIONAL LINE EMISSION RATE FACTORS

J. A. Fennelly, D. G. Torr

Center for Space Plasma and Aeronomic Research
University of Alabama in Huntsville
Huntsville, AL 35899

and

M. R. Torr

Space Science Laboratory
NASA Marshall Space Flight Center
Huntsville, AL 35812

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Abstract: The hydroxyl radical concentration in the stratosphere has been studied spectroscopically through observations of the ultraviolet multiple rotational lines in the $A^2\Sigma-X^2\Pi(0,0)$ vibrational band of OH (Torr et al., 1987). In order to infer the atmospheric distribution of OH, we have calculated the emission rate factors for selected rotational lines in the (0,0) band of the $A^2\Sigma-X^2\Pi$ electronic transition at wavelengths between 3076 Å and 3086 Å. In our calculations we have used the Einstein coefficients, line strengths, lower level energy and line positions of Goldman and Gillis (1980); the oscillator strength of Wang and Huang (1979); and the UV flux of the Sun from the Harvard Smithsonian sounding rocket flight of May 15, 1974, (Kohl et al., 1978).

INTRODUCTION

One of the processes forming the airglow in the Earth's atmosphere is the resonance reradiation of ultraviolet emission from the Sun by atmospheric atoms and molecules. Prominent among the molecules producing airglow, studied spectroscopically, is the hydroxyl radical. The hydroxyl radical, OH, is a very reactive species which controls many of the chemical processes in the atmosphere. For example, in the stratosphere OH plays a dominant role in moderating the destruction of ozone by partitioning of the odd-nitrogen and odd-chlorine compounds. Thus, due to this and other photochemical reactions with OH, the concentration of OH in the stratosphere has always been very important in our understanding of the region.

Data on OH concentration in the stratosphere are scarce.
Measurements of OH are difficult to acquire since spectral lines
of OH are hard to detect above the Rayleigh scattered sunlight
background. Measurements of the column content of OH have been
made from the ground in absorption using high resolution
interferometry (Burnett and Burnett, 1981; 1984). Also, Anderson
(1976) has measured OH column content by using an in situ
resonance fluorescence technique from 29 km to 43 km. The OH
concentration has been measured by using a balloon-borne LIDAR-
induced fluorescence experiment (Heaps and McGee, 1985). And
recently, Torr et al. (1987) have measured the OH concentration
using a high spectral-resolution, imaging, ultraviolet
spectrometer of a low light-scattering design to observe multiple
rotational lines of the OH $A^2\Sigma-X^2\Pi(0,0)$ vibrational band from a
balloon.

In this paper we report the results of a new calculation of
the emission-rate factors (also known as the g-factor) for the
brightest rotational lines in the (0,0) band of the $A^2\Sigma-X^2\Pi$
electronic transition at wavelengths between 3076 Å and 3086 Å.
These g-factors were used in the determination of the OH
concentration reported by Torr et al. (1987).

Anderson (1971) calculated the g-factor for the entire
OH(0,0) band by summing the individual rotational line g-
factors. However, Anderson (1971) did not report the individual
rotational line g-factors. As stated above, we have only
calculated g-factors for certain rotational lines in the OH(0,0)
band, not the entire band. Our calculations have been improved

over Anderson's (1971) by using an improved oscillator strength

value (Wang and Huang, 1980) and the Harvard Smithsonian solar

spectrum data (Kohl et al., 1978).

THEORY

Chamberlain (1961) developed the theory of resonance

scattering and fluorescence for an optically thin layer. He

expressed the emission rate of a specific vibrational band

transition in terms of the emission rate factor or simply the g-

factor. The emission rate is written as

$$4\pi \, I_{v'v''} = g_{v'v''} \, N_o/\mu \qquad (1)$$

where $4\pi \, I_{v'v''}$ is the emission rate (photons cm^{-2} sec^{-1});

$g_{v'v''}$ is the g-factor, the number of photons emitted per second

per molecule in the transition between the two vibrational levels

of v' and v''; N_o is the number of molecules in the column being

observed (molecule cm^{-2}); and $\mu = \cos\theta$, where θ is the angle of

emergence of the scattered photon. The v' denotes the

vibrational level of the upper electronic state and v'' the

lower. The molecule column density has the subscript o to

indicate the molecules are in the lowest vibrational level of the

ground state.

The g-factor between two vibrational levels of a molecule is

defined as

$$g_{v'v''} = \pi F_{ov'} \, [\pi e^2/mc^2] \, \lambda_{ov'}^2 \, f_{ov'} \, \frac{A_{v'v''}}{\sum_{v''} A_{v'v''}} \qquad (2)$$

where $\Pi F_{O\nu'}$ is the solar flux (photons cm^{-2} sec^{-1} A^{-1});
$[\Pi e^2/mc^2]$ is the electron radius; $\lambda_{O\nu'}$ is the wavelength of the
transition (A); $f_{O\nu'}$ is the band oscillator strength
(dimensionless); and $A_{\nu'\nu''}/\sum_{\nu''}A_{\nu'\nu''}$ is the albedo a for single-
scattering of the fluorescent band, where $A_{\nu'\nu''}$ is the Einstein
transition probability. The g-factor and the albedo are written
with the subscripts $\nu'\nu''$ which denotes they are in the
fluorescent band of emission whereas $O\nu'$ on the solar flux,
oscillator strength and wavelength indicates the absorption band
from the lowest vibrational level of the ground electronic state.

In this approximation various vibrational bands are
considered as individual units, without reference to the detailed
rotational structure of the bands. Pearce (1969) developed a
more complete model of the $A^2\Sigma-X^2\Pi$ electronic transition to
calculate g-factors by considering each vibrational band as
consisting of twelve rotational branches. He developed a formula
to calculate the individual rotational-line g-factor.

CALCULATION OF THE EMISSION RATE FACTOR (g-FACTOR)

The UV bands of OH are formed in emission from the
$A^2\Sigma-X^2\Pi$ electronic transition, where each vibrational band
consists of twelve rotational branches (see Figure 1). Following
Pearce (1969) and making well-founded assumptions, we write the
g-factor for a given rotation line of OH(0,0)

$$g[\theta, \nu', \nu'', J'', B] = \sum_{\nu JB}\left\{ \Pi F(\lambda[\nu', \nu, J, B])[\Pi e^2/mc^2]\lambda^2(\nu', \nu, J, B)f(\nu', \nu) \right.$$

$$\cdot \frac{S(J, B)}{\sum_{J^O}\sum_{B^O} 2J'(B)+1} N(\nu, J, i[B], \theta)\}$$

$$\cdot \frac{A(\nu', \nu'', J'', B'')}{\sum_{\nu^O}\sum_{J^O}\sum_{B^O} A(\nu', \nu^O, J^O, B^O)} \tag{3}$$

where θ is the rotational temperature (K), J is the total angular
momentum quantum number, B is the rotational branch index, S is
the rotationl line strength, N is the unity-normalized population
density for a given state, and i is the ground state doublet
index. An unprimed quantity refers to the ground state before
absorption, a primed quantity to the excited state, and a doubly
primed quantity to the ground state after reradiation.

It is assumed that the populations within the ground and
excited electronic states of the OH molecule are controlled
completely by collisions and radiation respectively. Also, it is
assumed that the Born-Oppenheimer approximation adequately
represents the OH molecule of J less than about 15. For the
wavelength range over which the g-factors are calculated, the J
values range from 1/2 to 11/2.

The unity normalized population densities are calculated on
the basis of the Boltzmann distribution since the first excited
electronic state of OH ($A^2\Sigma$) is not significantly populated by
collisions for temperatures less than about 600 K. The

assumption has been made that the various vibrational and rotational states of the electronic ground state are controlled completely by collisions. Thus, the unity normalized population is

$$N(\nu,J,i[B],\theta) = (2+J)\exp\{-[hc/k\theta]\ E(\nu,J,i[B])\}/Q(\theta) \qquad (4)$$

where $E(\nu,J,i[B])$ is the energy of the lower state energy, and $Q(\theta)$ is the partition function:

$$Q(\theta) = \underset{\nu J i}{\Sigma\Sigma\Sigma}\ (2J+1)\exp\{-[hc/k\theta]\ E(\nu,J,i[B])\}. \qquad (5)$$

As shown in Figure 1, OH molecules consist of two separate species during resonance reradiation: those which have positive or negative parity in the ground state. Herzberg (1950) states that transitions can only occur between states of opposite parity. Since the positive and negative parity states have equal weights, it is permissible to use a single expression for the populations.

The individual spectral-line parameters including line positions, strengths, Einstein coefficients, and lower-state energies are taken from Goldman and Gillis (1981) for the temperature $\theta=240$ K. In Goldman and Gillis (1981), the Einstein spontaneous emission coefficients are absolute, having been normalized on the basis of the lifetime measured by German (1974), $\tau=(0.688\pm0.007)$ $\times10^{-6}$ sec. This lifetime is for the

rotationless OH molecule for $v'=0$, $K'=2$, $J'=3/2$ quantum numbers. Since Chidsey and Crosley (1980) gives $A(v'=0,v''=1)/A(v'=0,v''=0)=0.0040$ and $A(v'=0,v''=2)/A(v'=0,v''=0)$ as vanishing, we have assumed that the vibrational level $v'=0$ makes negligible contributions to all ground vibrational states except the $v''=0$ state. Therefore, the summations over the ground vibrational states in equations (3) and (5) can be dropped.

The band oscillator strength for OH(0,0) was taken from Wang and Huang (1980). They reported $f_{00}=(1.09\pm0.04)\times10^{-3}$ without rotational excitation. When compared to the lifetime given by German (1974), it was found to agree very well. Also, Wang and Huang (1980) report an accuracy of better than ±4%.

The solar spectrum used was measured during a sounding rocket flight on May 15, 1974 [Kohl et al. (1978)]. Data were taken above 100 km so there was no significant atmospheric attenuation. Spectral resolution was 0.0028 nm. The systematic uncertainty in the absolute specific intensities is believed to be ±12%.

RESULTS AND CONCLUSIONS

We have calculated twelve g-factors which are listed in Table 1 along with their line positions, and their branches. These are the g-factors for the rotational lines used to infer the OH concentration reported in Torr et al. (1987). The g-factors for rotational lines reported here have an estimated accuracy of ±20%.

Acknowledgements.

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TABLE 1

EMISSION RATE FACTORS (g-FACTORS)

#	Wavelength(Å)	g-Factor	Branch(J')
1.	3084.053	5.71×10^{-6}	RR22(3/2)
2.	3083.380	3.32×10^{-6}	QP21(7/2)
3.	3083.280	9.76×10^{-6}	QQ11(9/2)
4.	3081.668	5.98×10^{-5}	PP11(3/2)
5.	3081.626	1.13×10^{-5}	QP21(5/2)
6.	3081.548	2.79×10^{-5}	QQ11(7/2)
7.	3080.238	1.00×10^{-5}	RR22(5/2)
8.	3080.012	1.25×10^{-5}	QP21(3/2)
9.	3079.957	3.16×10^{-5}	QP11(5/2)
10.	3078.476	4.58×10^{-5}	QP21(1/2)
11.	3078.443	4.91×10^{-5}	QQ11(3/2)
12.	3077.035	7.10×10^{-6}	RR22(7/2)

$A^2 \Sigma^2$

K' J'

4 9/2   +
   7/2   +

3 7/2   −
   5/2   −

2 5/2   +
   3/2   +

1 3/2   −
   1/2   −

0 1/2   +

$^O P_{12}$ P_{22} $^P Q_{12}$ Q_{22} $^Q R_{12}$ R_{22} P_{11} $^Q P_{21}$ Q_{11} $^R Q_{21}$ R_{11} $^S R_{21}$

K" J"   J" K"

6 11/2   +
                                                                 −

5 9/2   − +   11/2 5
                                                             + −

4 7/2   + −   9/2 4
                                                             − +

3 5/2   − +   7/2 3
                                                             + −

2 3/2   + −   5/2 2
                                                             − +

1 1/2   −   3/2 1
                                                               +

$X^2 \Pi_{3/2}$ $X^2 \Pi_{1/2}$

$J = K - \tfrac{1}{2}$ $J = K + \tfrac{1}{2}$
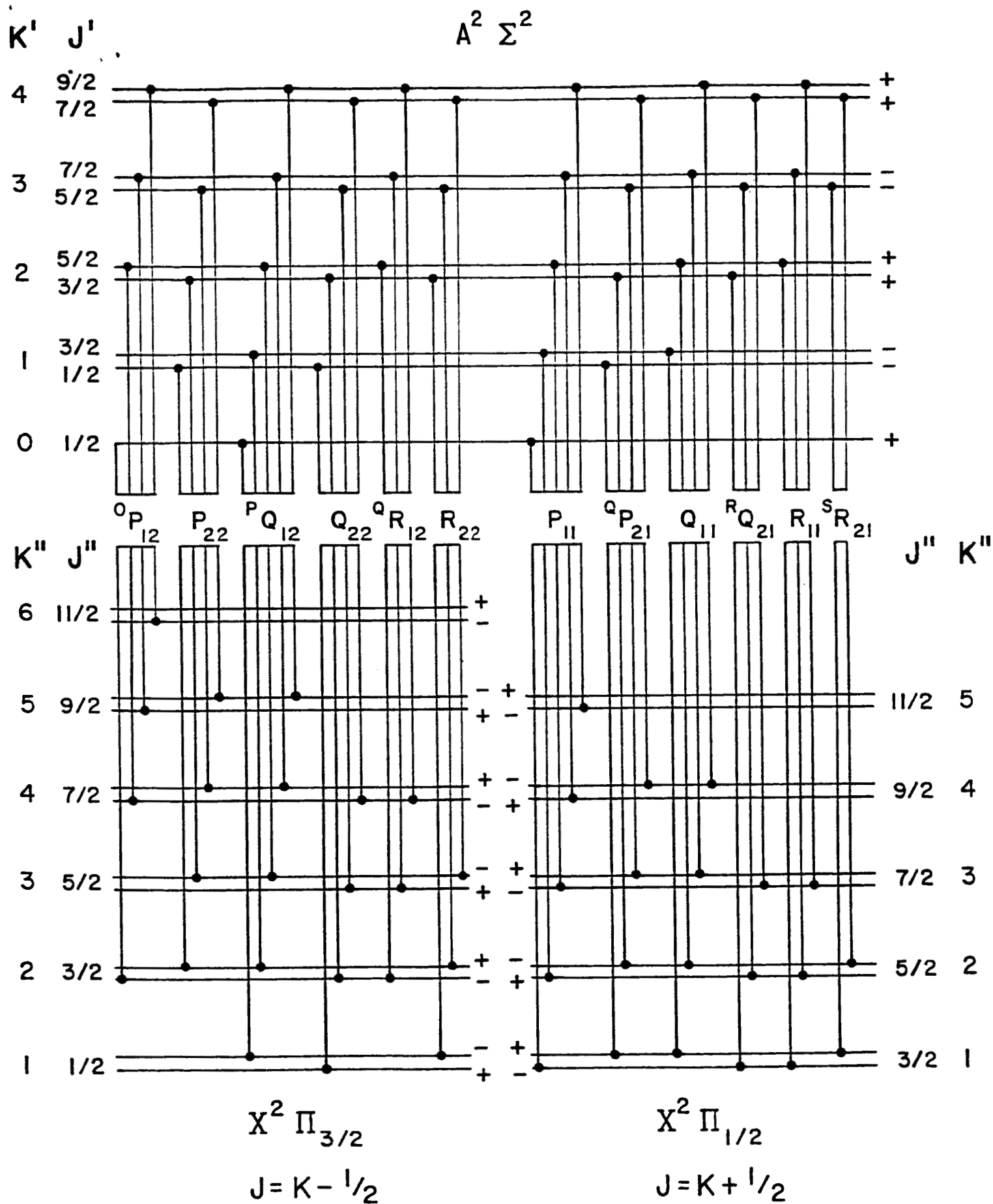
HYDROXYL MOLECULE ENERGY LEVEL DIAGRAM

FIGURE I